Miscibility and mechanical properties of a ternary blend of poly(3-hydroxybutyrate), polylactide, and cellulose esters

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ABSTRACT

Miscibility and mechanical properties of a ternary blend of poly(3-hydroxybutyrate) (P3HB)/poly (L-lactide) (PLLA)/cellulose esters (CEs) were investigated by X-ray diffraction, and dynamical mechanical analysis. The binary blend of P3HB and PLLA is generally immiscible if high molecular weight PLLA is used; however when only a small amount of 5 wt% cellulose esters such as cellulose acetate butyrate (CAB), cellulose acetate propionate (CAP), and cellulose propionate (CP) were added to the P3HB/PLLA blend, the crystallization of P3HB was significantly inhibited. Single glass transition temperature of P3HB/PLLA blends with 5 wt% cellulose esters was observed and can be fitted by Fox's equation extended to the ternary blend. This indicates that P3HB and PLLA are miscible when only 5 wt% cellulose ester, which acts as a compatibilizer, is added. The mechanical properties such as tensile modulus and elongation at break of (4/6) and (3/7) P3HB/PLLA blends with 5 wt% CP were almost identical to PLLA; however the maximum stress of these blend films was improved in comparison with the homopolymer. When 50 wt% CP was mixed to (7/3) P3HB/ PLLA blend, the elongation at break became 77.2%. Since CP inhibits the crystallization of P3HB, it can be assumed that this blend film shows ductility.

KEYWORDS: P3HB/PLLA/cellulose esters, ternary blend, miscibility, mechanical property.

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INTRODUCTION

One of the recent topics of interest in polymer science concerns renewable polymers obtained from natural resources such as plants and microorganisms. The biocompatible polymers can be obtained by biosynthesis from microorganisms as well as by enzymatic polymerization. Poly(3-hydroxyalkanoate) (P3HA) has received much attention as a degradable polymer obtained from microorganisms [1-3]. *Ralstonia eutropha* is well-known to accumulate poly(3-hydroxybutyrate) (P3HB). However, the stiffness and brittleness of P3HB due to high crystallinity have limited its practical application. In an attempt to improve the physical properties of this bacterial polyester, copolymers with different comonomer unit compositions such as 3-hydroxyvalerate [P(3HB-co-3HV] [4-7], and 3-hydroxypropionate [P(3HB-co-3HP)] [8-11] were biosynthesized, which resulted in a lower crystallinity compared to that of the P3HB homopolymer. The comonomer unit was regulated by using different carbon sources as a cultivation medium. In addition, block copolymer of P3HB and P3HBV was also biosynthesized [12-14]. The regulation of P3HB block is an important factor to determine the molecular morphology.

Another method for improving the physical properties of polymers is blending. Lots of polymers such as cellulose esters [15-23], poly(vinyl alcohol) [24, 25], and poly(lactide) [26, 27] have been investigated as components in a binary blend with P3HB. It has been reported that the cellulose esters of cellulose acetate butyrate (CAB), cellulose acetate propionate (CAP), and

cellulose propionate (CP) are miscible with P3HB, thereby improving the mechanical properties of the polymers.

Poly(L-lactide) (PLLA) is also known as a renewable polymer. There have been lots of investigations on its practical use, as well as on its academic interest. The physical properties of PLLA are compatible with those of polypropylene. Therefore, PLLA is highly anticipated as an alternate material to synthetic polymers originating from petrochemicals.

Investigation on binary blends of P3HB and PLLA has been carried out by Doi *et al.* who reported that P3HB is immiscible with a high molecular weight of PLLA [28]. In this paper, we prepared the P3HB/PLLA blending with cellulose esters as a compatibilizer, and the miscibility and mechanical properties were investigated by X-ray diffraction and mechanical analysis.

MATERIALS AND METHODS

Poly(L-lactide) was supplied by Shimadzu Co. Ltd. The L content was 98%. P3HB and cellulose esters of CAB and CP with $M_n = 7.0 \times 10^5$ and 7.0×10^5, respectively, were purchased from Aldrich Chemical Co. Ltd. CAP with $M_n = 7.5 \times 10^4$ was purchased from Kanto Chemical Co. Ltd. CAB has a content of butyryl (37%), acetyl (13%), and hydroxyl (9.7%) groups, and CP has a content of propionyl (38%) group. CAP has a content of propionyl (46%), acetyl (2.5%), and hydroxyl (1.8%) group.

Blend films were prepared as follows. First PLLA, P3HB, and the cellulose ester were dissolved in hot chloroform to obtain a homogeneous solution, and then cast on a glass plate to evaporate chloroform. After heating the cast film in a hot press at 200 °C, the film was quenched in ice water. The measurements were carried out after maintaining the films at room temperature for more than 7 days.

Wide-angle X-ray diffraction patterns were recorded on an automatic diffractometer (RIGAKU RINT2500) with Ni-filtered Cu Kα radiation (40 kV and 200 mA). Dynamical mechanical measurements were performed with a DVA-200 (ITK Co., Ltd.) at a frequency of 10 Hz and a heating rate of 3 °C. Tensile properties were measured by INSTRON5566.

An initial gauge length of 15 mm and a testing rate of 0.5 mm/min were used.

RESULTS AND DISCUSSION

X-ray diffraction patterns of P3HB/PLLA with 5 wt% cellulose esters

In order to get clarity on the effect of addition of cellulose ester for the P3HB/PLLA system, a binary blend film of P3HB/PLLA was first investigated. Figure 1 shows X-ray diffraction patterns of a binary blend of PLLA and P3HB quenched from the melt. For the PLLA, the melt-quenching process allows the formation of an amorphous state. With increasing P3HB content, strong and sharp diffraction peaks were observed around 13° and 17°. These diffraction peaks are assumed to be (020) and (110) of the crystalline P3HB, respectively. At lower P3HB content, the diffraction peaks of crystalline P3HB were reduced, but still observed. This indicates that the PLLA and P3HB were immiscible throughout the whole blending ratio and the crystallization of P3HB was not inhibited by PLLA. As described in the introduction, it has been reported that the cellulose esters inhibit the crystallization of P3HB. Therefore, we attempted the addition of cellulose esters to the P3HB/PLLA blend and confirmed the miscibility. Figure 2(A), (B), and (C) show the X-ray diffraction patterns of P3HB/PLLA blend films with 5 wt% of CAB,
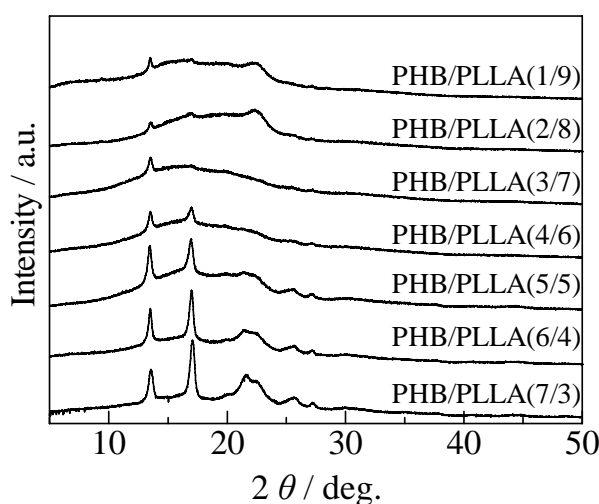
Figure 1. X-ray diffraction patterns of a binary blend of P3HB/PLLA.
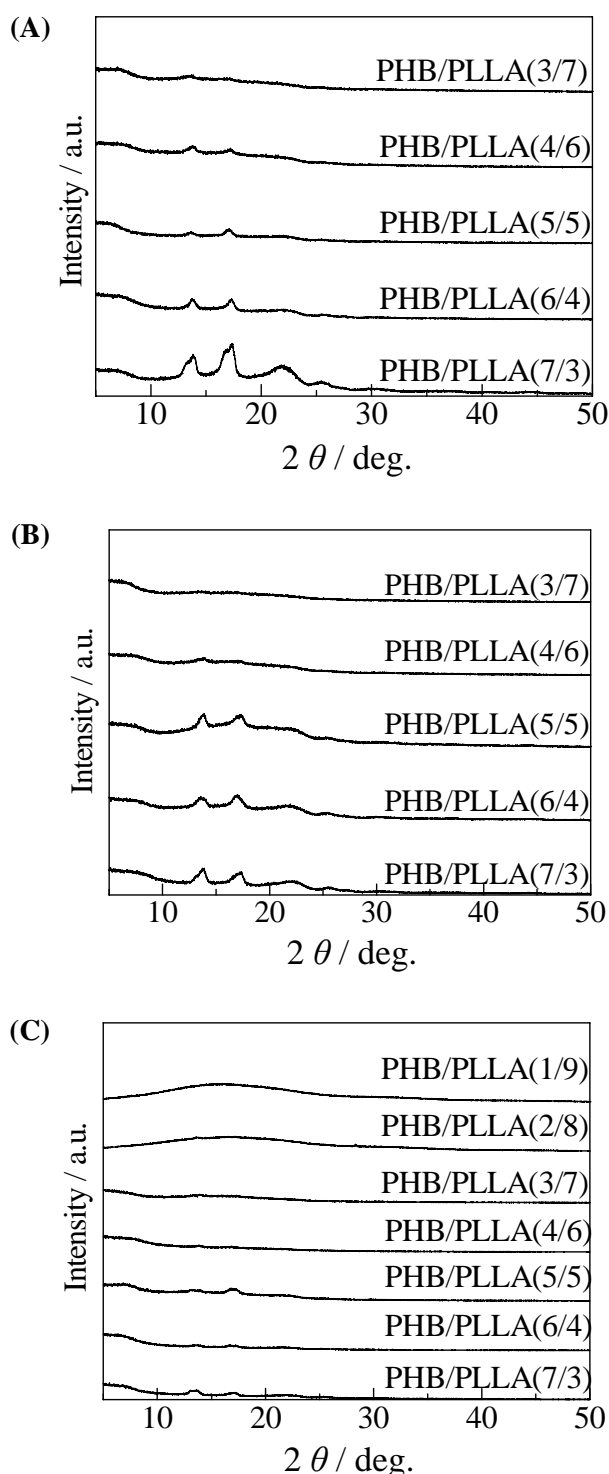
(A)

(B)

(C)

Figure 2. X-ray diffraction patterns of a ternary blend of P3HB/PLLA/cellulose esters. 5 wt% of cellulose esters was blended for each film. The blend ratio of P3HB and PLLA is represented in the figure. (A), (B), and (C) show the blends with CAB, CAP, and CP, respectively.

CAP, and CP, respectively. The P3HB/PLLA ratio was changed from 1/9 to 7/3. By adding these cellulose esters, the diffraction peaks corresponding to the crystalline P3HB were very small or almost absent. This shows that the crystallization is significantly inhibited by cellulose esters. For the blend film with CAB and CAP shown in Figures 2(A) and (B), the diffraction pattern shows a typical non-crystalline pattern for low P3HB content, but some peaks corresponding to the crystalline P3HB were observed for high P3HB content. This shows that the crystallization of P3HB can be effectively inhibited at low P3HB content. It was suggested that P3HB and PLLA would be miscible when assisted by cellulose esters such as CAB and CAP. Since the crystallization of P3HB was observed for high P3HB content, P3HB chains would aggregate by phase separation during the melt-quenching process and crystallize in the P3HB-rich region. When CP was used as shown in Figure 2(C), no diffraction peak corresponding to the crystalline P3HB was observed irrespective of the P3HB content. This shows that CP is the most suitable material for inhibiting the crystallization of P3HB among the cellulose esters used in this investigation.

Miscibility of the ternary blend of P3HB, PLLA, and cellulose esters

In order to get clarity on the miscibility of these blend films, dynamical mechanical analysis was carried out. Figure 3 shows the storage modulus, E', and the mechanical loss tangent, tan δ, for P3HB/PLLA with 5 wt% cellulose esters. All blend films showed a sharp peak for tan δ between 40 and 70 °C irrespective of the cellulose esters used. These peaks are assumed to be the glass transition temperature (T_g). If the blend film is immiscible, three T_g's corresponding to each polymers would be observed; however, these ternary blend films provided a single T_g for low P3HB content. This shows that these blend films are miscible in the non-crystalline region. The T_g's of these blend films are plotted in Figure 4 as a function of P3HB content. The T_g for low P3HB content was around 70 °C, which is identical to that for PLLA. With increasing P3HB content, T_g was reduced. The semi-empirical equation of T_g for a miscible blend has been reported by Fox [29]. This equation is generally employed to the
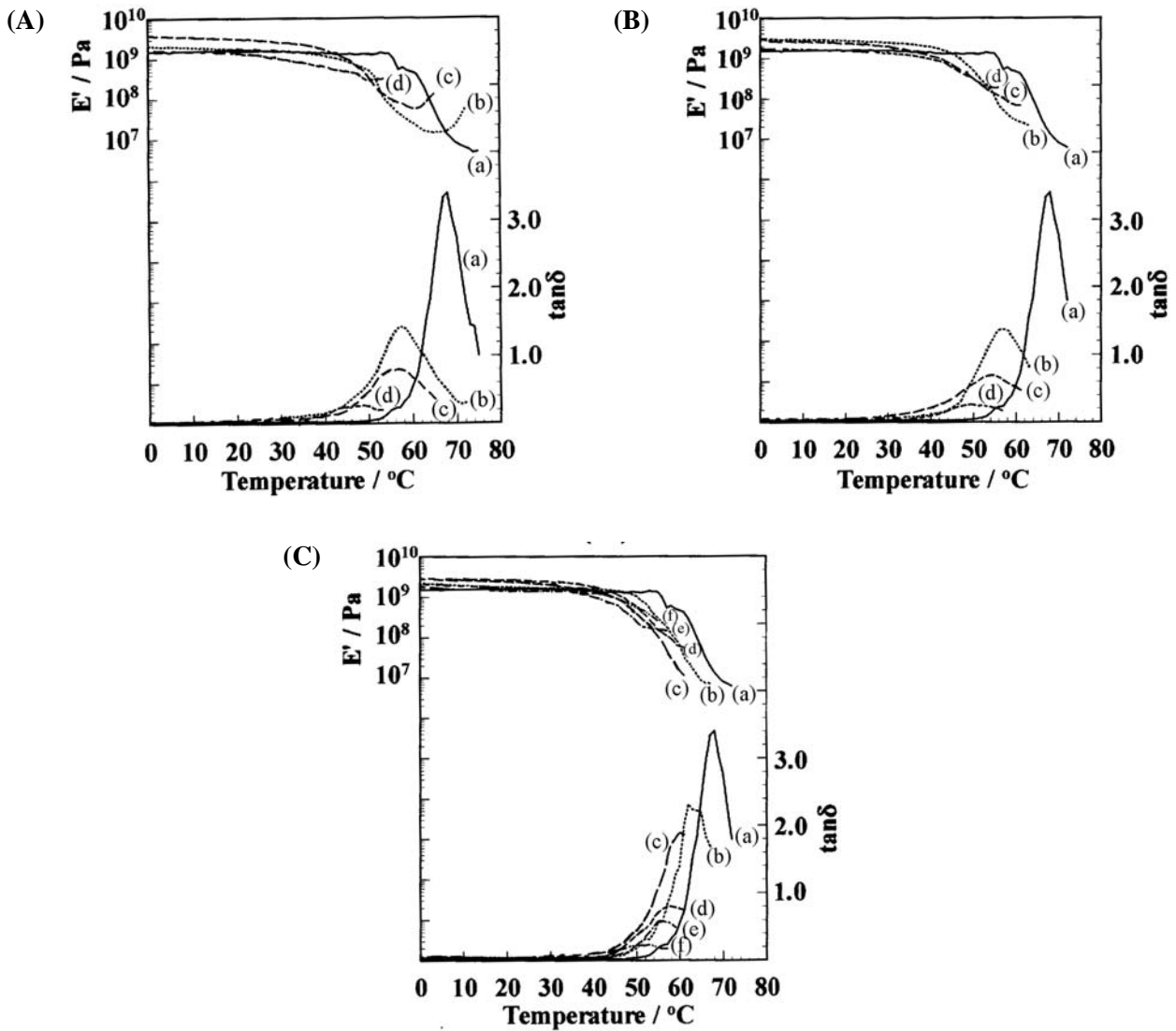
(A)

(B)

(C)

Figure 3. Dynamic mechanical spectra of a ternary blend of P3HB/PLLA/cellulose esters. 5 wt% of cellulose esters was blended for each film. (A), (B), and (C) show the blend with CAB, CAP, and CP, respectively.

—— (a) PLLA; ·········· (b) (1/9); — — — (c) (2/8); - - - - (d) (3/7); — · — (e) (4/6); — · · — (f) (5/5).

binary blend system. Some of researchers applied this equation to the ternary blend system and succeeded in obtaining good agreement between experimental values and the theoretical curve [30]. Therefore, we attempted to extend the Fox equation to a ternary blend system as follows:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \frac{W_3}{T_{g3}} \qquad (1)$$

where W_n and T_{gn} are the weight fraction and glass transition temperature of components n = 1, 2,

and 3, respectively. The curve shown in Figure 4 represents the theoretical curve estimated by equation (1). Good agreement was obtained between experimental and theoretical curves. This indicates that this ternary blend system is miscible in the non-crystalline region. As described in the 'Introduction', P3HB is basically immiscible with PLLA. However, the addition of only 5 wt% cellulose ester made miscibility possible between P3HB and PLLA. Therefore, these cellulose esters can be used as a compatibilizer for a P3HB and PLLA blend.
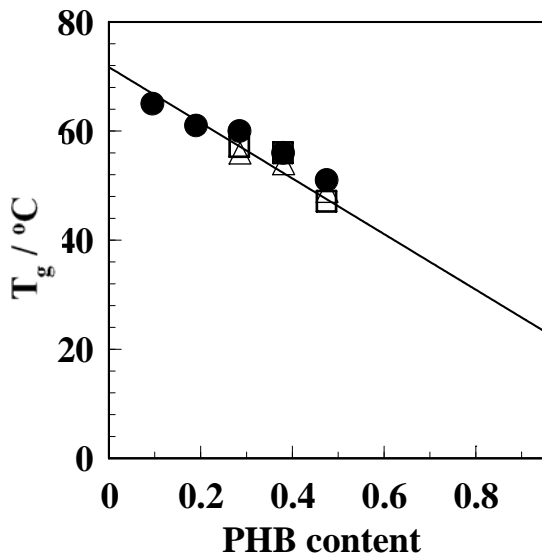
Figure 4. Dynamic mechanical glass transition temperature of a ternary blend of P3HB/PLLA/cellulose esters as a function of P3HB weight fraction. □ : CAB; Δ : CAP; and ● : CP. The solid curve was calculated by equation (1).

Figure 5. Stress-strain curves of PLLA and a ternary blend of P3HB/PLLA/CP. 5 wt% of CP was blended for P3HB/PLLA with (4/6) and (3/7) weight ratio.

- - - - (a) PLLA;   – · –   (b) (4/6);   ——— (c) (3/7);
········ (d) P3HB.

Mechanical properties of P3HB/PLLA/CP blends

Figure 5 shows the stress-strain curve of PLLA and ternary blend films. The (4/6) and (3/7) P3HB/PLLA blends with 5 wt% CP, which featured low crystallinity and good miscibility, were used in this measurement. Tensile modulus, elongation at break, and maximum stress are listed in Table 1. The tensile modus of ternary blend films for P3HB/PLLA (3/7) and P3HB/PLLA (4/7) with 5 wt% CP were almost identical to that of PLLA, but smaller than that of P3HB. Concerning the maximum stress, it was improved by adding 5 wt% CP in comparison with homopolymers. The maximum stress of PLLA and P3HB were 20 and 21 MPa, but that of the films with 5 wt% of CP were 25 and 28 MPa. These films are so hard that the elongation at break was only a few percent. Maekawa *et al*. reported that the binary blend of P3HB/CP with 50 wt% CP is elongated to more than 90% [31]. Therefore, we measured the mechanical property of P3HB/PLLA/CP ternary blends with 50 wt% CP. Figure 6 shows the stress-strain curve for (4/6) and (7/3) P3HB/PLLA blends with 50 wt% of CP. The yield point was observed for ternary blend films, which show ductility. As for the (7/3) blend film
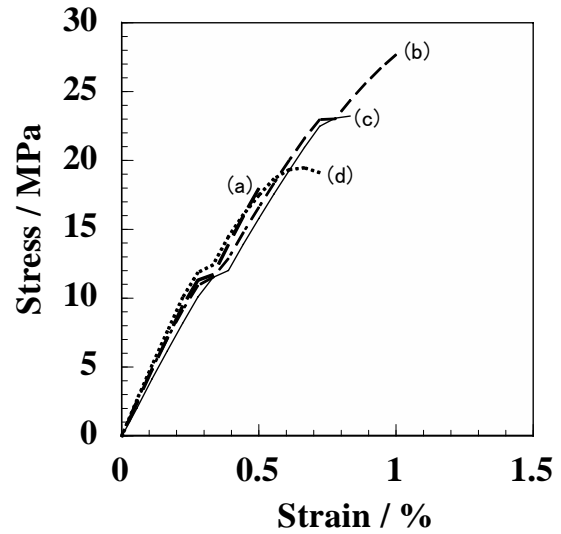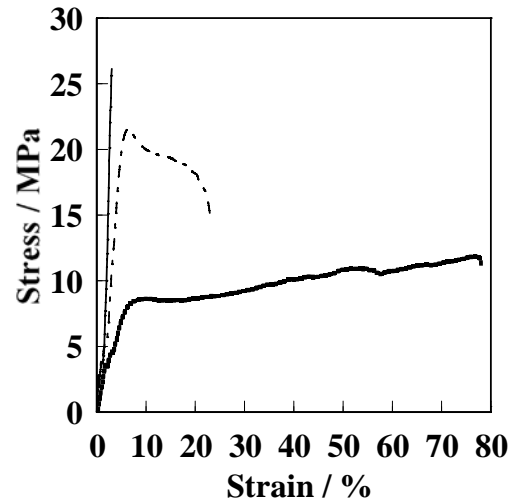

Figure 6. Stress-strain curves of PLLA and a ternary blend of P3HB/PLLA/CP. 50 wt% of CP was blended for (4/6) and (7/3) P3HB/PLLA blend.

——— PLLA;   – · – · –   (4/6) blend with 50% CP;
■■■ (7/3) blend with 50% CP.

with 50 wt% CP, the film was highly elongated. The mechanical properties of the blend films with 50 wt% CP are also listed in Table 1. A quite remarkable result is the behavior of the (7/3)

Table 1. Tensile properties of PLLA, P3HB, and ternary blends of P3HB/PLLA/CP.

	Tensile modulus/ GPa	Elongation at break/ %	Maximum stress/ MPa
PLLA	1.8	3.2	20
P3HB	2.7	4.3	21
P3HB/PLLA(3/7) with 5 wt% of CP	1.8	3.2	25
P3HB/PLLA(4/6) with 5 wt% of CP	1.6	3.0	28
P3HB/PLLA(4/6) with 50 wt% of CP	0.71	23.7	23
P3HB/PLLA(7/3) with 50 wt% of CP	0.31	77.2	12

blend film with 50 wt% CP, which showed a significant increase in ductility. An elongation of greater than 77% was achieved. The tensile property is presumably dominated by the non-crystalline region, which is regarded as a soft segment. Therefore, this can be explained by the decrease in crystallinity of the blend film. It was concluded that the mechanical properties of maximum stress and elongation at break can be improved depending on the amount of CP added to the P3HB/PLLA blend.

CONCLUSIONS

The miscibility and mechanical properties of a ternary blend of P3HB, PLLA, and cellulose esters were investigated by X-ray diffraction and mechanical analysis. It was found that the crystallization of P3HB was significantly inhibited by adding 5 wt% cellulose esters such as CAB, CAP, and CP, though the crystallization of P3HB was promoted for the binary blend of P3HB and PLLA. It is worth noting that a small amount of CP significantly inhibited the crystallization of P3HB. The T_g of P3HB/PLLA blend film with 5 wt% cellulose esters can be fitted by the extended Fox's equation. This indicates that the cellulose ester acts as a compatibilizer for the P3HB/PLLA blend and as a result these ternary blends were miscible. The tensile modulus and elongation at break of (4/6) and (3/7) P3HB/PLLA blend films with 5 wt% CP were almost identical to those of PLLA. However, the maximum stress was improved by mixing 5 wt% CP. When 50 wt% CP was mixed for (7/3) P3HB/PLLA blend film, elongation greater than 77% was achieved. The reduction of

crystallinity of P3HB allowed the elongation at break to be larger.

CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest.

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